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CALORIMETRIC STUDY OF HYDROGEN IN Zr - 2.5 Wt% Nb PRELIMINARY REPORT

Report No. 87-41-K

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ABSTRACT

Preliminary results of a calorimetric study of hydrogen in Zr-2.5 wt% Nb pressure tube alloys are presented. Two samples with 84 ppm and 14 ppm hydrogen were examined. The terminal solid solubility temperatures (TSS_p: the temperature at which hydride precipitation begins and TSS_d: the temperature at which hydride dissolution is complete) were measured for the 84 ppm H sample and the TSS_d was determined for the 14 ppm H sample. Good agreement with literature values was obtained for the measured values of TSS_d for both the 14 and 84 ppm H samples. The disparity which was observed for the TSS_p values requires further investigation. Nondestructive laboratory determinations for hydrogen appears feasible by correlating the total enthalpy change measured with predetermined hydrogen concentrations. The technique requires further investigation into the degree of quantification possible.

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84-538-051	823.21	March 19, 1987	87-41-K

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EXECUTIVE SUMMARY

CALORIMETRIC STUDY OF HYDROGEN IN Zr - 2.5 Wt% Nb
PRELIMINARY REPORT

K.M. Tashiro

Objective: To develop a technique for determining the terminal solid solubilities and concentration of hydrogen in Zr-2.5 wt% Nb pressure tube alloys.

Key Results:

1. Calorimetry has been shown to be a feasible method for the determination of the terminal solid solubility (TSS) temperatures of hydrogen in zirconium pressure tube material. There are two TSS temperatures of importance; TSS_p which represents the temperature at which hydride precipitation commences and TSS_d which represents the temperature at which hydride dissolution is complete. This technique has been shown to exhibit the following characteristics:

   (a) The technique has sufficient sensitivity to detect hydride dissolution and to determine the TSS_d temperatures for samples with as little as 14 ppm hydrogen.

   (b) The TSS_d and TSS_p temperatures for an 84 ppm hydrogen sample have been determined with good reproducibility.

   (c) Small sample size (<100mg) and minimal sample preparation are required.

2. Nondestructive hydrogen concentration determinations are possible with this method to levels as low as 14 ppm hydrogen.

3. There is sufficient sensitivity to detect an annealing anomaly on the first heating of a sample. This anomaly appears to affect the TSS_d temperature observed.

Recommendations:

The preliminary results presented here indicate that a further comprehensive study of hydrogen in zirconium pressure tube material by calorimetry is required. Further research will concentrate on the reproducibility of TSS values and attempt to determine the source of any disparity observed. Quantitation of the calorimetric curve for hydrogen determinations will also be performed.

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To Dr. D. Mills
Director of Research

CALORIMETRIC STUDY OF HYDROGEN IN Zr - 2.5 wt% Nb
PRELIMINARY REPORT

1.0 INTRODUCTION

The deleterious effects of hydrides upon the mechanical properties of zirconium alloy pressure tube material are well documented. The effects of hydrides mainly manifest themselves in the nucleation and growth of blisters, delayed hydride cracking and loss of fracture toughness at low temperatures. It is therefore desirable to be able to characterize these processes as much as possible. The minimum information required for characterization is:

(a) Accurate and precise hydrogen concentrations of the tube material.

(b) The terminal solid solubility temperatures (TSS_p: the onset temperature of hydride precipitation, TSS_d: the temperature of complete hydride dissolution) of hydrogen in Zr - 2.5 wt% Nb alloys for irradiated and non-irradiated conditions. Unfortunately, TSS values for irradiated material are lacking.

(c) The growth or dissolution rate (kinetics) of hydrides for a given set of conditions. In addition, this includes factors such as hydrogen diffusivity and heat of transport Q^* (for blister growth).

The principles and instruments used for calorimetric measurements are briefly described. The report considers conventional methods for determining hydrogen concentration and TSS temperatures and then concentrates upon the specific applications of calorimetry for determining these quantities. The precision and accuracy of calorimetric determinations of these quantities are considered as well as its applications to irradiated materials.

2.0 CALORIMETRY

Calorimetry is a technique in which changes in thermal properties are measured. Heat capacity is the usual property determined by measuring the changes in enthalpy in the sample. There are two basic types of calorimeters, the dynamic adiabatic calorimeter and the differential calorimeter as described in Appendix A. Differential calorimetry is a technique in which differential changes in enthalpy between a sample and reference are measured. Enthalpy changes may have numerous sources but are often the result of phase transformations in the sample. The precipitation and

dissolution of zirconium hydride is an ideal transformation for study by calorimetry since it occurs over a temperature range well within the capabilities of most instruments and the transformation is relatively rapid as compared to other solid state phase transformations.

The enthalpy changes are determined by measuring the differential heat flow between the sample and a reference. There are two techniques used to measure this heat flow. The first is Calorimetric Differential Thermal Analysis (CDTA) and the second is Differential Scanning Calorimetry (DSC). CDTA determines the heat flow indirectly by measuring the temperature differences between the sample and reference. DSC determines the heat flow directly. A description of each technique is given in Appendix A.

Under ideal conditions, the heat flow Q(t) developed during a phase transformation can be estimated by:

$$Q(t) = m\Delta H_t \, (dC/dt) \quad (W) \qquad (1)$$

where ΔH_t is the enthalpy of transformation ($J/g/at\%_H$) for the specific product phase formed, m is the sample mass (g) and (dC/dt) is the overall reaction rate ($at\%_H/s$). The reaction rate is dependent upon the kinetics of the reaction and the heating (or cooling) rate. The lowest detectable heat flow, sample mass and the magnitude of ΔH_t will determine the slowest heating rate possible. The total enthalpy is determined by integrating the heat flow over time.

3.0 HYDROGEN CONCENTRATION MEASUREMENTS

At present, the two major techniques employed for direct hydrogen measurement in zirconium pressure tube material are vacuum effusion and nuclear reaction analysis. Vacuum effusion extracts the hydrogen from a heated sample and then measures the quantity of extracted hydrogen gas by one of a number of methods such as thermal conductivity. This method is destructive to the sample and is subject to a substantial amount of experimental scatter. Nuclear reaction analysis utilizes high energy particles to induce nuclear reactions with hydrogen and is nondestructive to the sample. The products of this reaction are then detected and correlated with the amount of hydrogen present. A small probe size can give the technique good spatial resolution. However, the nuclear reaction occurs at small depths into the material (<10 microns) and could therefore be sensitive to surface segregation effects. Additionally, sample analysis costs are high since instrument costs are also high.

The ideal hydrogen determination technique would possess the following properties:

(1) High precision
(2) High accuracy
(3) Small sample size and minimal preparation
(4) Nondestructive to the sample
(5) Low cost per analysis
(6) Bulk measurement

Calorimetry is a promising technique to develop as it has the potential to offer all of these properties that the other techniques do not.

The area under the peak of the calorimetric signal is related to the total amount of energy released (or absorbed) during precipitation (or dissolution) of hydrides in the zirconium sample. A hydrogen determination is possible since the energy measured is related to the total amount of hydrogen that has participated in the reaction and the amount of hydrogen remaining in solid solution at ambient temperatures is very small. Given a calorimetric response as shown in Figure 1, the hydrogen concentration is determined by:

$$C_H = (1/mR) \int_{T_L}^{T_H} [Q(T) - B(T)]/\Delta H_t \, dT + C_H(T_L) \quad (at\%_H) \qquad (2)$$

where; m is the sample mass (g), R is the heating or cooling rate (°C/s), Q(T) is the calorimetric signal (W/g), B(T) is the background response (W/g), ΔH_t is the enthalpy of transformation ($J/g/at\%_H$) and is specific to the hydride involved (i.e. ΔH_t for zirconium delta hydride and gamma hydride will differ (as well as for titanium hydrides)). The offset $C_H(T_L)$ is the solid solubility of hydrogen at the lower temperature limit ($at\%_H$). This offset is required as a definite amount of hydrogen remains in solution at the lower temperature limit and is not detectible as it has not participated in the phase transformation.

The major sources of error in the determination are as follows: B(T), Q(T), $C_H(T_L)$ and ΔH_t. The error associated with the background response B(T) is related to the stability of the calorimeter. The background is interpolated between the beginning and end of the transformation in order to establish the boundaries for integration. The interpolated background parameters are determined by the operator and are therefore highly subjective. As the background curvature or system noise increases, the background becomes more difficult to model correctly which increases the error in the integration. The calorimetric signal Q(T) error is mainly dominated by noise. In order to decrease this error, the signal to noise ratio must be increased. This can be accomplished by utilizing greater heating (or cooling) rates which increases the heat flow. However, since calorimetric stability usually degrades at higher rates, a compromise rate (which is dependent upon the specific calorimeter) must be utilized.

The heat of transformation, ΔH_t and the lower offset concentration $C_H(T_L)$ are complex parameters which are dependent upon the actual physical processes that occur during the phase transformation. These processes are expected to depend on the rate of temperature change, the sample's thermal history, microstructure and irradiation damage. Therefore, ΔH_t and $C_H(T_L)$ may not be uniquely defined for a given hydrogen concentration. This ambiguity is expected to be prevalent at lower hydrogen concentrations where the processes may be complicated by the presence of gamma hydride.

4.0 DETERMINATION OF THE TERMINAL SOLID SOLUBILITY TEMPERATURES (TSS_p and TSS_d)

A number of different techniques have been used to determine the terminal solid solubility of hydrogen in zirconium pressure tube material. By far the most common techniques used/1/ are: dilatometry, crack initiation detection, internal friction effects, resistivity and diffusion equilibrium. A problem common to all of these methods is the accurate determination of the

hydrogen concentration that correlates with the measured TSS temperature. Each technique possesses individual difficulties which affect the precision and accuracy of the determination. These difficulties are as follows:

(1) Dilatometry, internal friction effects and resistivity: These methods produce curves similar to that shown in Figure 2. The difficulty arises since the position of the discontinuity that defines the transition temperature is subject to error.

(2) Crack initiation detection can only determine TSS_p. In addition for detection of a crack, the hydrides must have grown to sufficient size. The transition temperature may also be modified by the presence of stress.

(3) Diffusion equilibrium techniques usually only determine TSS_d. Under certain experimental conditions, stress is also present and may modify the transition temperature.

Calorimetric determination of the terminal solubility temperatures also has its difficulties. The major problem is that the technique is a dynamic one. Therefore, the temperatures determined by this techniques are not the equilibrium temperatures. There are two processes that will affect the accuracy of the measured temperatures: hydride precipitation and dissolution kinetics and heat transfer characteristics to the sample.

Poor heat transfer to the sample results in the sample temperature lagging behind the measured temperature. Poor heat transfer will result if the thermal contact resistances to the sample are excessive. This effect can be minimized by using slower temperature ramp rates and reducing the thermal contact resistances. These resistances can be minimized by using samples with large contact areas and not using sample holding pans during measurement.

If the kinetics are rapid and heat transfer to the sample is good, the determined temperatures are a good estimation of the equilibrium temperatures. This will hold true mainly in the high temperature region where the volume diffusivity is high enough to allow rapid equilibration. However, at low temperatures, these conditions will not exist. The process will lag behind the changing equilibrium point due to slow kinetics. It is still possible to determine the equilibrium temperature by correcting for the effects of kinetics either mathematically or by utilizing a slower ramp rate.

There are a number of different methods in which to define TSS_p and TSS_d from the calorimetric data. Shown in Figure 3 are the main conventions for temperature definition. The first method is the maximum peak height method and it usually represents the point of maximum heat evolution (or absorption). The second method is the point of departure. This is the point of the first discernible changes in enthalpy. At low temperature change rates, this method establishes the equilibrium temperature well. This method relies heavily upon the background modeling and is therefore subject to large errors and irreproducibility. The last method is known as the onset method. This method estimates the point of departure temperature. The temperature is the point where the interpolated baseline and the 50% peak tangent intersect.

5.0 PRELIMINARY CALORIMETRICS RESULTS AND DISCUSSION

An early calorimetric study was performed by Bussiere et. al./2/ on high hydrogen concentration Zr - 2.5 wt% Nb samples. The effects of hydride dissolution were discernible, however, the results were not quantified extensively. In addition, a large background signal was obtained which represents the heat capacity of the sample itself.

The main objective of this study is to quantify the calorimetric signal as much as possible. In order to facilitate quantitation, the large background signal due to sample heat capacity effects is removed by balancing the calorimeter with a reference. The reference consists of a Zr - 2.5 wt% Nb specimen of nearly the same mass but with most of the hydrogen removed.

Extensive sample preparation was found not to be necessary. Samples were approximately 100 mg in weight with dimensions of 1 x 4 x 4 mm. Samples were measured calorimetrically then submitted for hydrogen determination by the vacuum effusion technique.

Typical calorimetric heating curves for 84±8 and 14±3 ppm hydrogen samples are shown in Figures 4 and 5 respectively. Figure 6 is a calorimetric cooling curve for the 84 ppm H sample. The temperature hysteresis is apparent when compared to the heating curve for the same sample given in Figure 4. Heating backgrounds are relatively stable which facilitates peak area determinations. However, this stability is lost for cooling curves. Improved instrument operation is required in order to alleviate this instability.

A summary of the results for 84±8 and 14±3 ppm hydrogen samples are shown in Table 1. The peak areas for the 84 and 14 ppm H samples are 2.42±.03 J/g and 0.24±.06 J/g respectively for a heating rate of 50°C/min. The relative experimental scatter observed represents approximately 3 ppm H and 4 ppm H respectively. If quantitation of hydrogen by peak area measurement is feasible, then calorimetry provides a more precise method of hydrogen determinations. However, since calibration must be performed with standards measured by the vacuum effusion technique, the precision and accuracy of the calorimetric measurements will be determined by the accuracy of the effusion technique.

The zirconium hydride's heat of transformation ΔH_t has been determined from the experimental data for each sample heated at the rate of 50°C/min. The calculated values are 28.7 ±0.3 kJ/mole H for the 84 H ppm sample and 16.3±1.1 kJ/mole H for the 14 ppm H sample (neglecting hydrogen concentration error). A large disparity is found when these values are compared to the value found by Brooks et. al. for 55 ppm H in Zircaloy 2 of 38.6 kJ/mole H. This value was determined by adiabatic calorimetry which is characterized by very low heating rates (<5°C/min). This disparity may be a result of the heating rate and concentration dependence of ΔH_t as referred to previously.

The effects of different heating rates are also summarized in Table 1. Generally, the heating rate affects the integrated peak area. As the heating rate increases, the peak area increases. This variation in peak area is normally observed in DTA measurements and can be calibrated out in CDTA measurements. In addition, there is the possibility that the peak area decrease is the result of an underlying thermodynamic process that affects the amount of heat liberated which will depend upon the heating rate. An opposite effect is seen in the cooling curve enthalpies, however, the unstable background as shown in Figure 6 makes these determinations unreliable.

The measured values of TSS_d and TSS_p for the 84 and 14 ppm H samples are compared to literature values as given in Table 2. Good agreement is generally observed except for the TSS_d values determined by Erickson and Hardie/7/ for pure zirconium. This disparity is believed related to the low strength of pure zirconium as described by Puls/9/. However, another effect which can cause a shift in TSS_d has been observed and will be considered later. It is generally found in the literature that TSS_d values are reproducible. However, TSS_p values are subject to a considerable amount of experimental scatter. This reflects the premise that the hydride precipitation process is actually very complex and is being modified by various metallurgical factors. A few examples of metallurgical factors which can affect precipitation are: hydride nucleation on phase interfaces/10/ and misfit dislocation nucleation/9/.

Agreement for the 14 ppm H sample TSS_d value is considered fortuitous since experimental data at these low concentrations is not as extensive and most of the data for these concentrations are derived from high concentration extrapolations. TSS values at low concentrations require further quantification.

The effects of ramp rate upon the transition temperatures is also shown in Table 1. Generally, there is a shift of the transition temperature to lower values when a change in the ramp rates from 50 to >10°C/min occurs. From the limited experimental data, it appears that the temperature shift is similar for both the 84 ppm and 14 ppm samples at a heating rate of 50°C/min. Therefore, it is believed that the major component of this temperature shift is due to heat transfer effects to the sample with dissolution kinetics effects playing a minor role.

Figure 7 illustrates an anomaly that occurs when the sample is heated for the first time. An endothermic prepeak presents itself well before the hydride dissolution peak. Fortunately, this peak only occurs once and the calorimetric curves afterwards are reproducible. The origin of this feature is unknown at this time. The prepeak is suggested to involve the hydride dissolution process since it has resulted in an increase in the observed TSS_d temperature. If it were an independent process, the TSS_d temperature would not be affected. The determination of the characteristics and origin of this feature is necessary in order to verify its effect upon TSS_d values since it could result in observed values that are too high. Therefore, a study of the effects of thermal history upon TSS_d values is also warranted.

It is concluded that for quantitative determinations of hydrogen concentration and the TSS temperatures, a precise set of experimental conditions must be used in order to establish the values of ΔH_t and $C_H(T_L)$. In order to decrease errors, hydrogen determinations should be performed at high heating rates for greater peak area and TSS determinations at low heating rates to decrease shifts due to heat transfer and kinetic effects.

Calorimetry can be useful in the investigation of irradiated zirconium pressure tube material. It is well suited for investigating irradiated material since the sample size is small, sample preparation is minimal and the technique is sensitive to weak thermal events. If metallurgical factors affect the onset of hydride precipitation, then TSS measurements of irradiated material will be necessary. Unfortunately, TSS information for irradiated material is scarce at this time. Calorimetry should be able to monitor the processes involved in annealing of irradiation damage, however this process may also alter the results of TSS temperature evaluations especially if defect-hydrogen interaction is appreciable.

6.0 SUMMARY

Differential scanning calorimetry has been shown to exhibit the following advantages:

A. Quantitative hydrogen concentration measurements appear possible once a standard measurement and calibration technique have been established to determine ΔH_t and $C_H(T_L)$ over the concentration range desired.

B. The terminal solubility temperatures have been established for 84±8 ppm H (TSS_d = 333 ±4°C and TSS_p = 270±2°C) and for 14±3 ppm H (TSS_d = 213±3°C) samples with good precision utilizing the onset temperature definition. Good agreement with literature values have been obtained.

C. Calorimetry has shown it possesses sufficient sensitivity to detect hydride dissolution at low hydrogen concentrations and weak thermal events such as the heating prepeak as shown in Figure 7.

D. Measurements can be made on small samples (typically on the order of 100 mg) without a large amount of special preparation. This makes it suitable for TSS evaluations of irradiated material.

E. The measurements are nondestructive to the sample unlike vacuum fusion methods for hydrogen determinations. Since multiple measurements can be performed on a sample, precision can be improved.

F. Since calorimetry is a thermal method, the study of the effects of thermal history upon TSS values and the enthalpy of transformation can be easily performed.

The disadvantages of the method are:

A. Whereas, vacuum fusion techniques can be applied to hydrogen in any base metal without extensive recalibration, calorimetric determination of hydrogen concentration is specific to the hydride formed. Recalibration is necessary if different hydrides are produced since the chemical heat of transformation ΔH_t and the lower concentration limit $C_H(T_L)$ differs for each base metal species.

B. Being a dynamic measurement method, full static chemical equilibrium is never achieved. This will have its greatest effect in the determination of the TSS temperatures. However, fast kinetics at high temperatures (>250°C) and lower heating or cooling rates can be utilized in order to minimize the error in the TSS temperatures.

7.0 RECOMMENDATIONS

1. Calorimetry has been shown to be a viable method for; determining the concentration of hydrogen in Zr - 2.5 wt% Nb alloys, determining the upper and lower terminal solid solubility temperatures (TSS_d and TSS_p) and detecting weak thermal events which can modify hydride dissolution processes. It is suggested that a full comprehensive study be performed in order to ascertain the precision and accuracy of hydrogen determinations and TSS evaluations by this technique. Such measurements would require the highest

possible amount of sensitivity and reproducibility. Therefore, reliable access to a single user calorimeter may be required. A comprehensive research program would require a large number of sample measurements in order to determine the following:

(a) Reproducibility of TSS_d and TSS_p for samples with similar thermal history and microstructure.

(2) The effects of different thermal history and microstructure on the TSS values. Specific processes to be tested are: different heating and cooling rates prior to measurement, high temperature annealing and cold working of the sample.

(3) Investigation of the observed prepeak and any other detected weak thermal events.

(4) Quantitation of the peak area for hydrogen determinations and the effects of the above mentioned processes on peak area.

(5) A similar study using irradiated material.

8.0 ACKNOWLEDGEMENTS

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TABLE 1
Summary of Calorimetric Results for Zr - 2.5 wt% Nb Samples

H Conc ppm	Ramp °C/min	Run #	Peak Area J/g	Peak Temp °C	Onset Temp °C
84	+50	03/07/30	2.43	307.8	337.0
		11/07/21	2.41	305.6	332.6
		12/07/21	2.41	305.8	333.3
		07/08/05	2.44	307.9	336.6
	+20	01/08/01	1.85	306.3	331.0
		02/08/01	1.84	305.1	333.3
		06/08/05	1.78	308.6	332.3
	+10	03/08/05	1.44	304.2	331.0
84	-15	04/07/30	1.92*	262.5	270.2
		05/07/30	2.00*	264.1	271.3
	-10	02/07/30	2.41*	262.8	269.5
14	+50	08/07/21	0.27	189.1	214.0
		09/07/21	0.21	185.4	212.3
		13/07/21	0.23	188.1	214.8
		14/07/21	0.24	184.3	213.0
	+5	05/08/05	0.11	183.5	206.8

* - Backgrounds were difficult to model accurately, therefore peak areas are subject to considerable error

TABLE 2
Summary of TSS Values

Sample	84 ppm H		14 ppm H
	TSS_d °C	TSS_p °C	TSS_d °C
Present work (Zr - 2.5 Nb) (Calorimetry)	334±4	270±2	213±3
Byrne and Leger/6/ (Zr - 2.5 Nb) (Compilation)	335	271	205
Slattery/8/ (Zircaloy-2) (Dilatometry)	331	261	204
Erickson and Hardie/7/ (Zirconium) (Dilatometry)	349	275	247

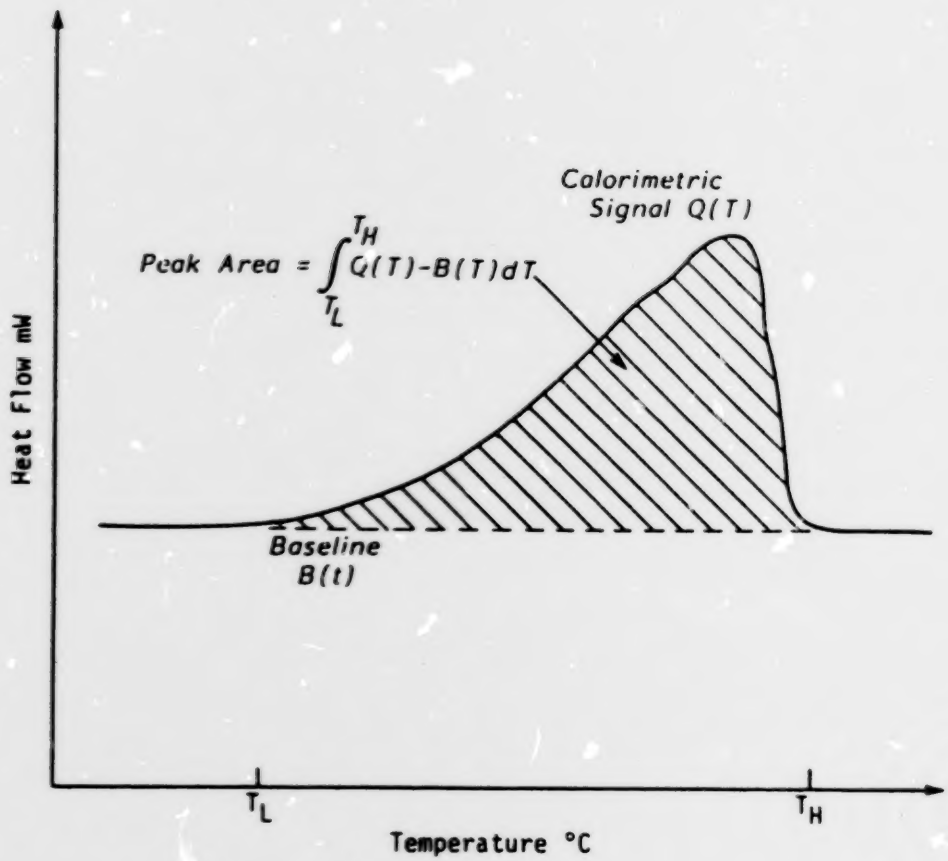


Figure 1 Quantification of the calorimetric curves. Quantification of the curve requires the modelling of the background B(T) and subsequent integration of the peak area defined by Q(T) and B(T).

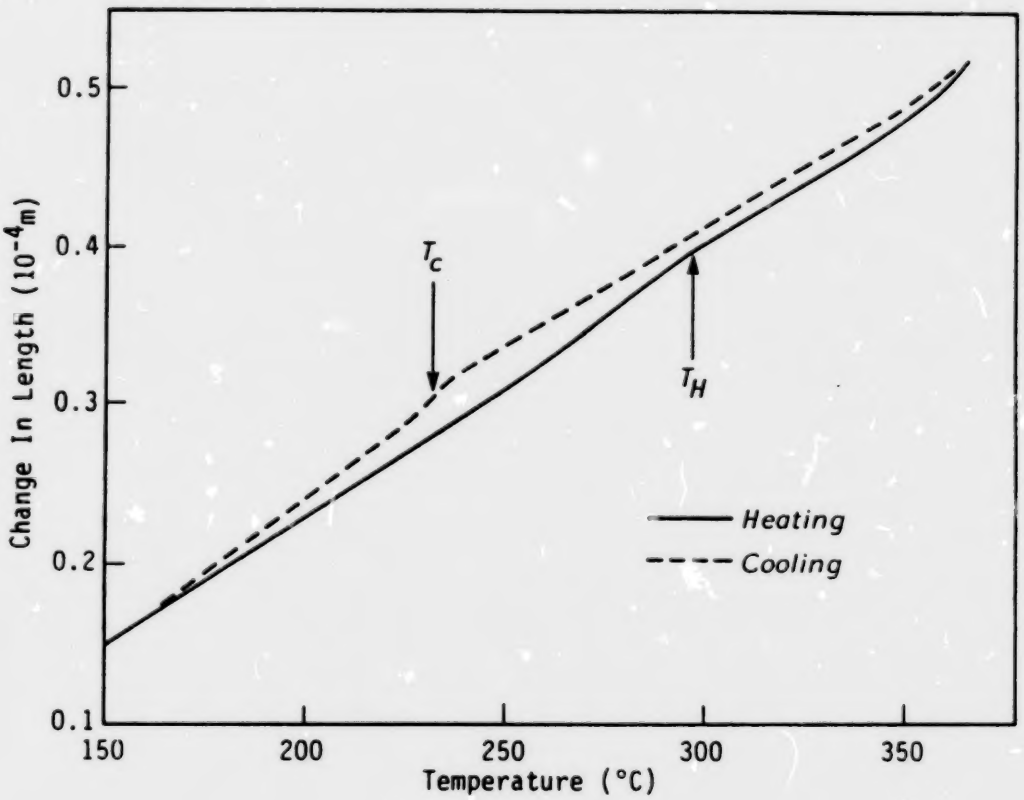


Figure 2 TSS determination by dilatometry for a Zr - 2.5 wt% Nb sample containing 60 ppm H/4/. This curve is typical to those obtained by dilatometry, internal friction effects and resistivity. Errors arise from the position of the discontinuity which defines TSS.

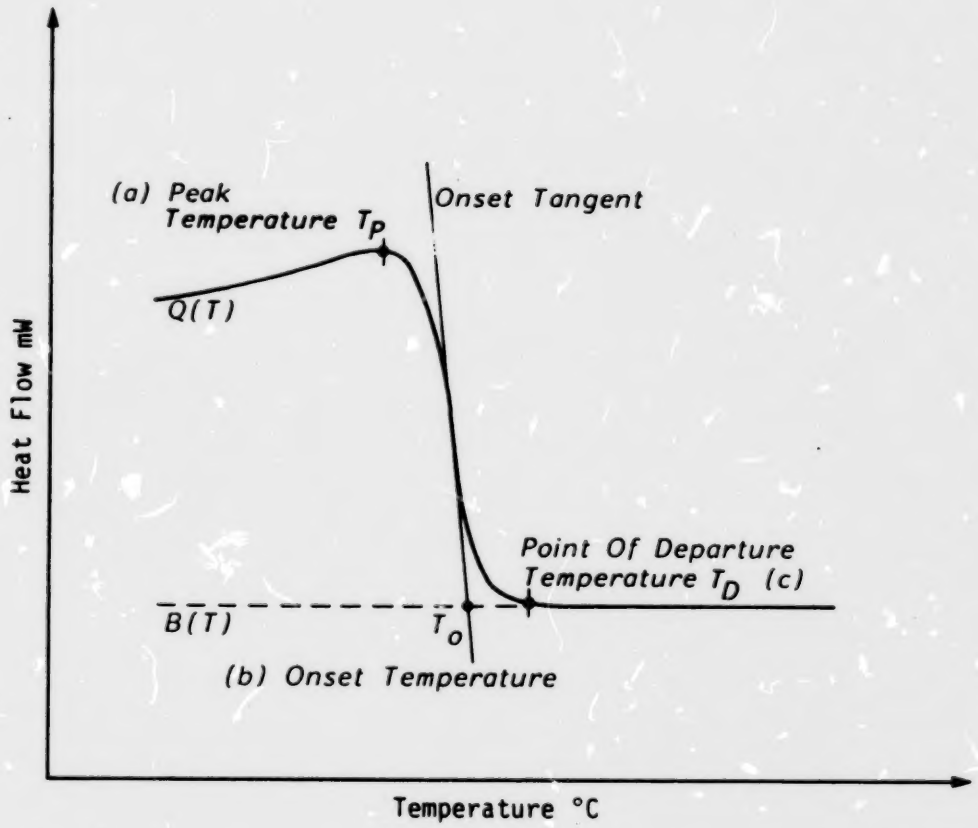


Figure 3 Conventions utilized in defining transition temperatures. The three methods use to define the transition temperature are:
(a) the peak temperature
(b) the onset temperature
(c) the point of departure temperature

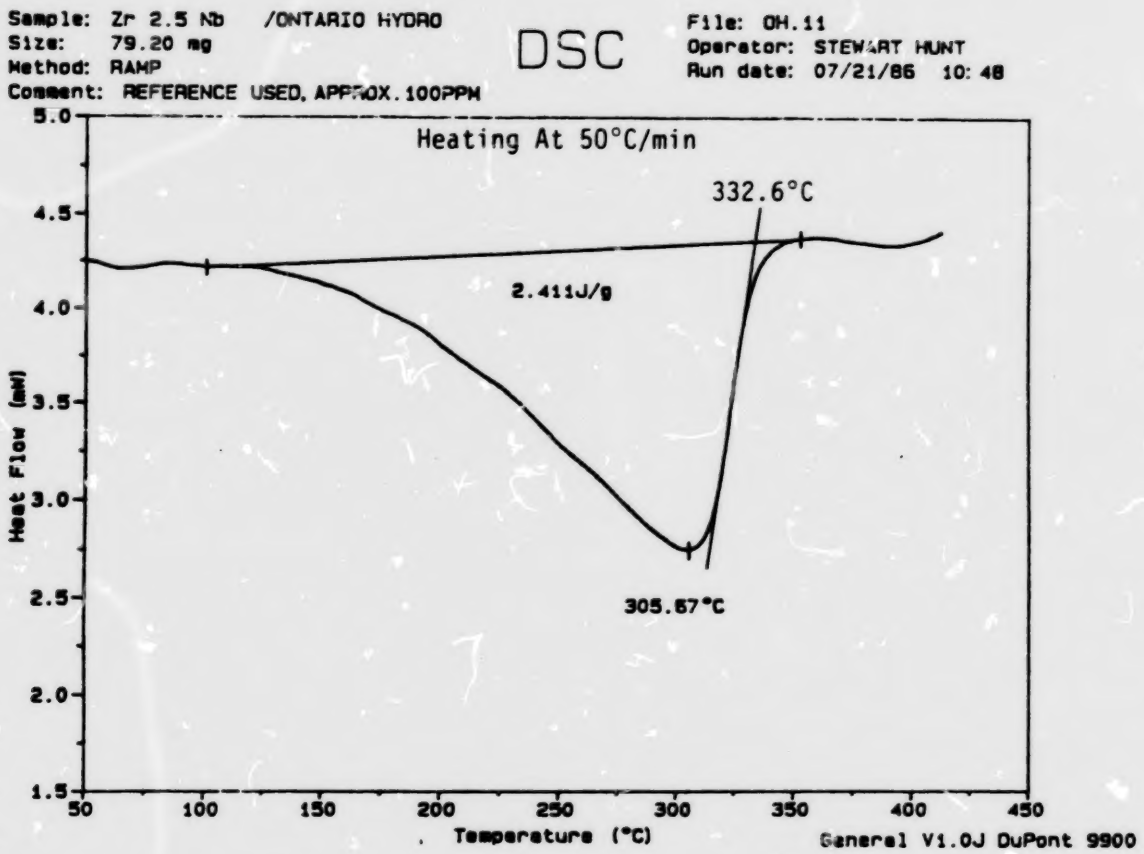


Figure 4 Calorimetric curve for a Zr - 2.5 wt% Nb sample.
Hydrogen concentration: 84 ppm
Heating rate: 50°C/min

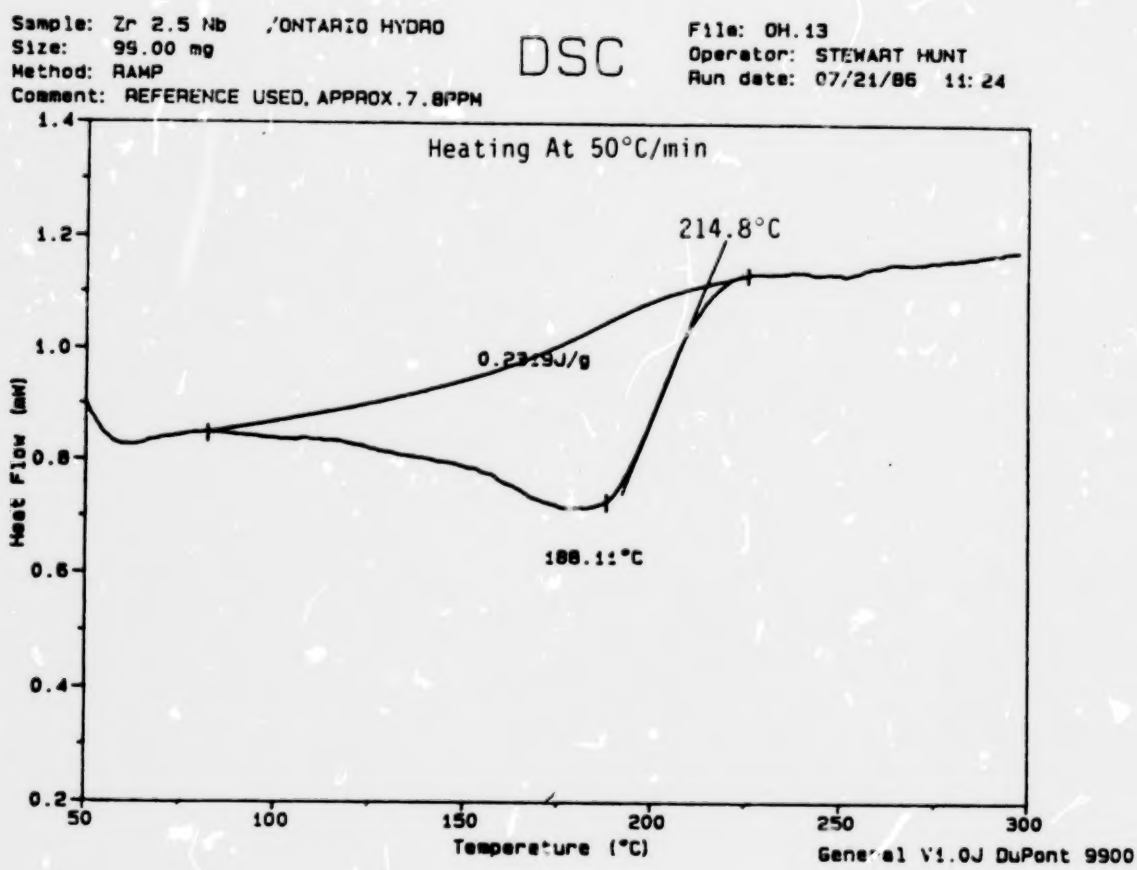


Figure 5 Calorimetric curve for a Zr - 2.5 wt% Nb sample.
Hydrogen concentration: 14 ppm
Heating rate: 50°C/min

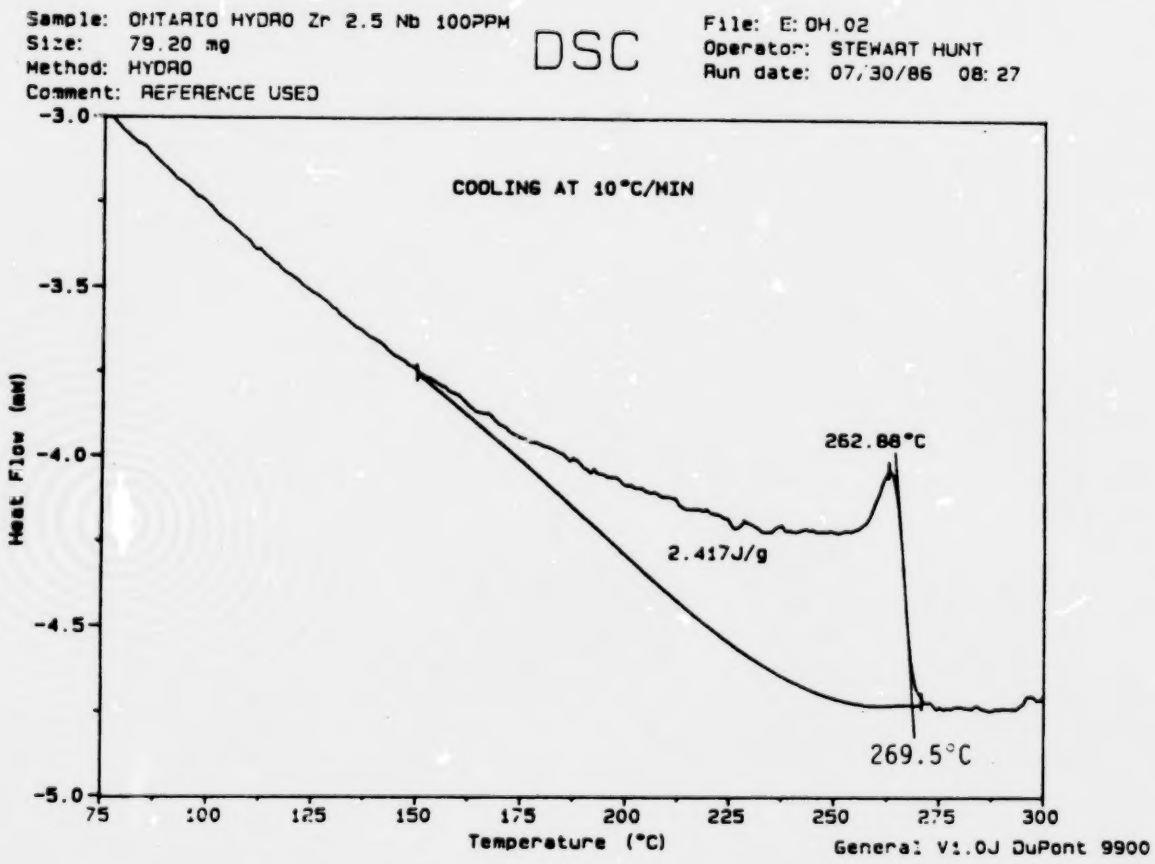


Figure 6 Calorimetric curve for a Zr - 2.5 wt% Nb sample.
Hydrogen concentration: 84 ppm
Cooling rate: 10°C/min
Poor baseline stability inhibits precise enthalpic determination. However, temperature hysteresis is prominent as compared to the heating curve of Figure 4.

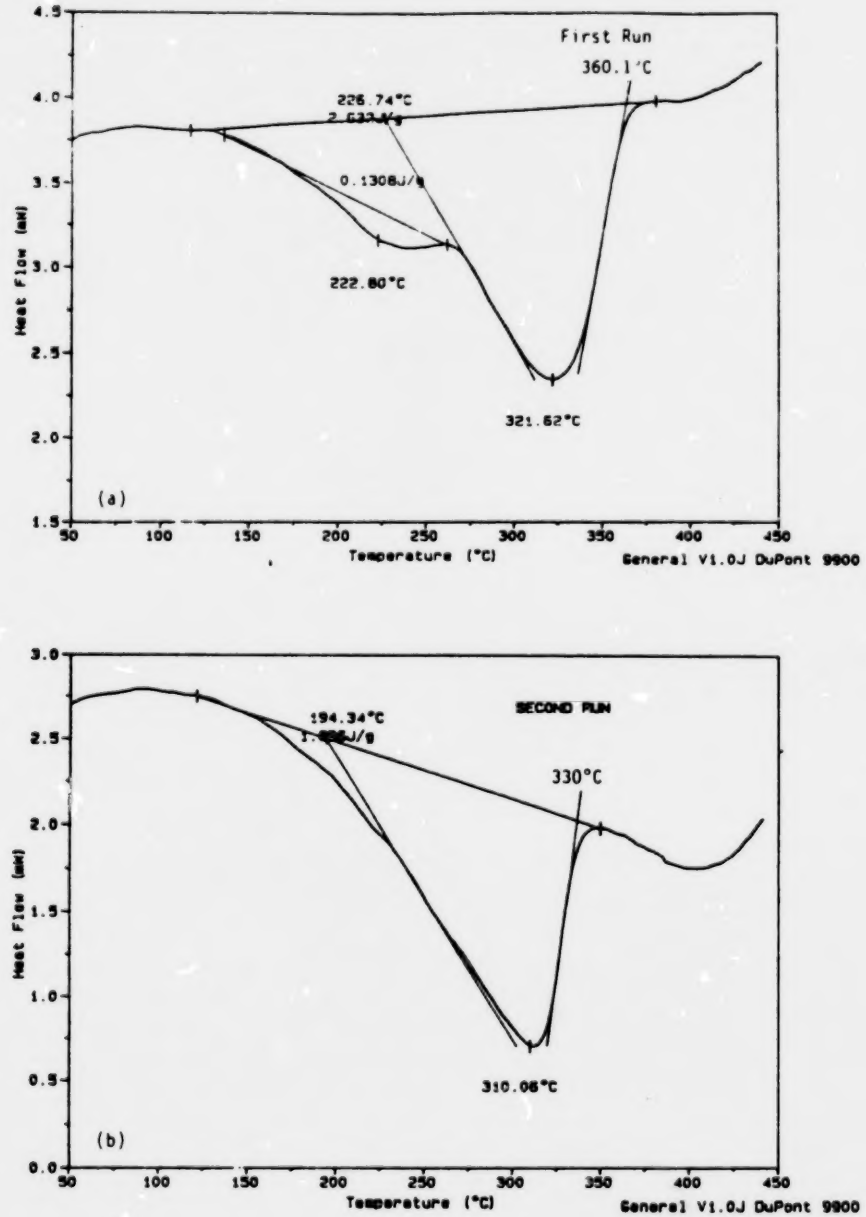


Figure 7 Annealing anomaly in a Zr - 2.5 wt% Nb sample.
Hydrogen concentration: 84 ppm
Heating rate: 50°C/min
(a) illustrates the endothermic heating prepeak
(b) illustrates the subsequent heating measurement with the disappearance of the prepeak
A shift in the TSS_d temperature is evident from 360°C to 330°C on subsequent heating.

APPENDIX A
Calorimetric Thermal Analysis

Calorimetric thermal analysis is based on the detection of changes in enthalpy. These changes in enthalpy are as result of the heat capacity of the sample, changes in the heat capacity or phase transitions that occur within the sample as the temperature changes. Measurement of enthalpy changes fall into two basic categories, dynamic adiabatic calorimetry and differential calorimetry.

A dynamic adiabatic calorimeter as shown in Figure A1 measures the sample's enthalpy changes under conditions of complete thermal isolation (adiabatically). This is accomplished by minimizing the temperature difference between the sample and the adiabatic jacket by controlling the outer furnace jacket. Only the outer jacket should lose any appreciable amount of heat. The sample temperature is made to rise at a specific rate by an auxiliary heater and the heat flow to the sample is recorded. A typical calorimetric measurement for 55 ppm H Zircaloy 2 is shown in Figure A2. The sample points represent the heat capacity of the alloy without hydrogen whereas the solid line is with hydrogen. The heat required by the dissolution of the hydride is superimposed upon the alloy's heat capacity curve. Small changes in enthalpy due to weak phase transformation are difficult to resolve since the large heat capacity of the sample results in less then optimum operating conditions.

Differential calorimetry measures the differences in enthalpy between a sample and a reference. Small thermal events can be recorded since the large sample heat capacity effect can be minimized by utilizing an inert reference which possesses a similar heat capacity. Therefore, the calorimeter can operate at maximum sensitivity. There are two basic types of differential calorimeters: calorimetric differential thermal analyzers (CDTA) and differential scanning calorimeters (DSC). Heat flow between the sample and the reference is the experimental quantity desired.

CDTA instruments are a specialized form of differential thermal analyzers (DTA) which are essentially temperature responding devices. The differences between the classical DTA instruments and the calorimetric DTA instruments are shown in Figure A3. Classical DTA places the sample and reference in contact with a large thermal mass (heating block) and locates the measuring thermocouples within the specimens. This method allows the determination of transition temperatures but since the heat loss to the block is unknown, only semi-quantitative determinations of the total enthalpy change is possible. Calorimetric DTA instruments do not utilize a heating block and places the thermocouples outside of the specimens. Additionally, the instruments are designed such that there is one major heat flow path between the sample and reference. The heat flow is determined indirectly by placing a thermocouple junction near this main heat flow path and measuring the temperature difference. A small error in transition temperature is incurred since the temperature of the sample holder and not the actual sample temperature is measured. Modern instruments with computer aided calorimetric corrections easily approach DSC instruments in accuracy.

DSC instruments measure the differential heat flow directly. The sample and reference are thermally isolated as shown in Figure A4 and auxiliary heaters heat the specimens at a predetermined rate and maintain the temperature difference between them to zero. The difference in heat flow is determined by the difference in the power supplied to each individual heater. The auxiliary heaters are controlled by a feedback control system which is characterized by a slow response time. Therefore, fast transitions can be distorted or missed entirely.

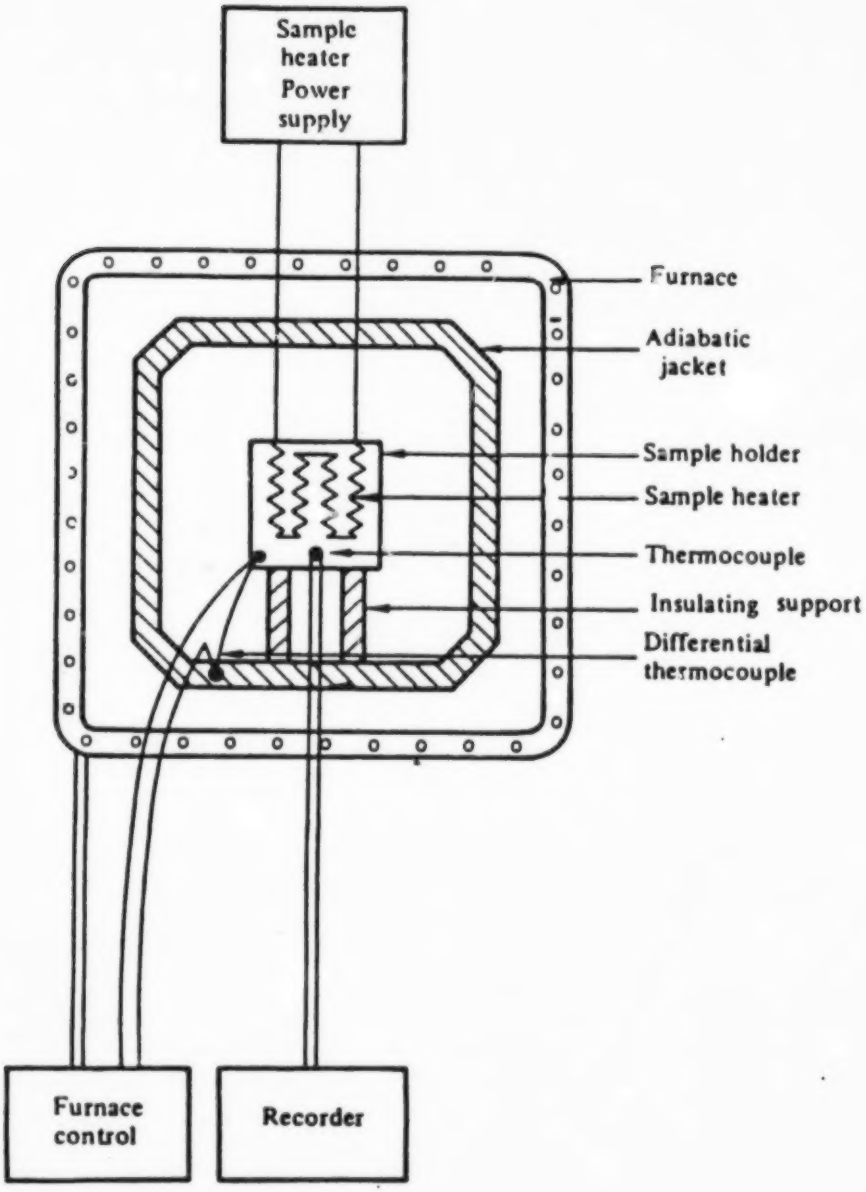


Figure A1 Dynamic adiabatic calorimeter /5/. The adiabatic jacket and outer temperature are held to the same temperature. Therefore, only the jacket loses heat. The heat flow is determined by having constant heat input and measuring the temperature changes or maintaining the temperature ramp constant and measuring the required heat input.

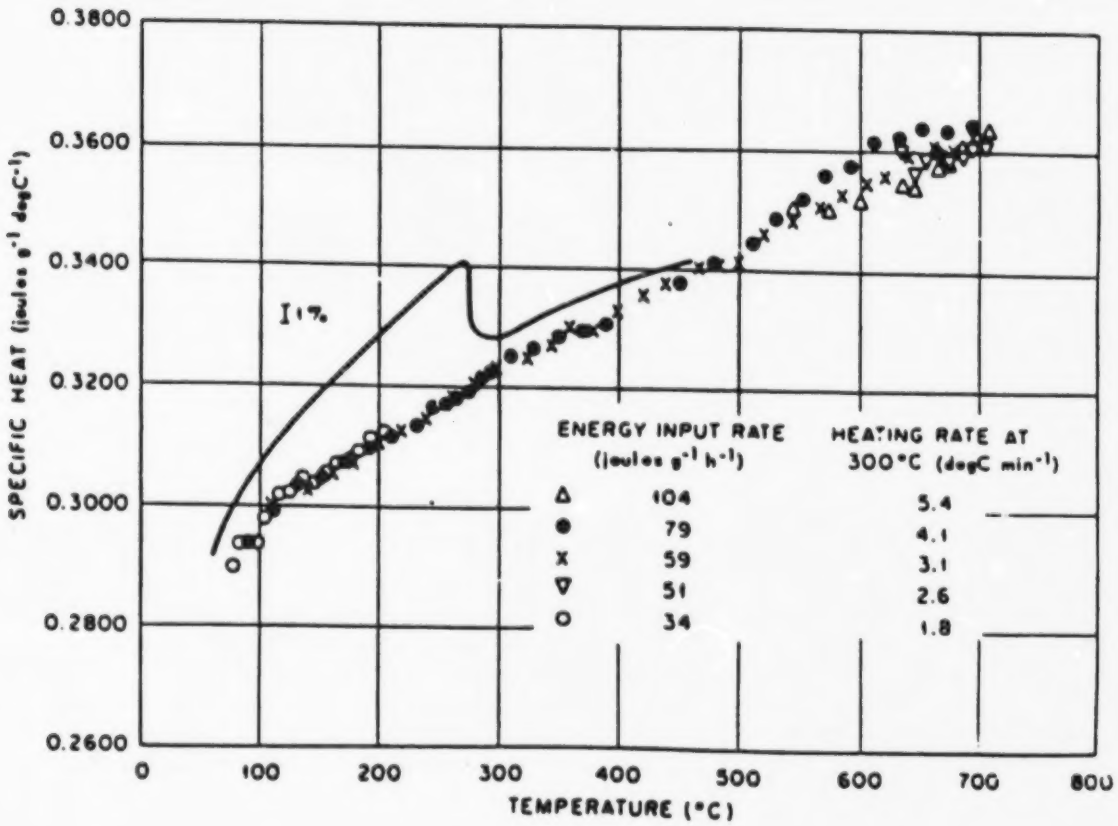
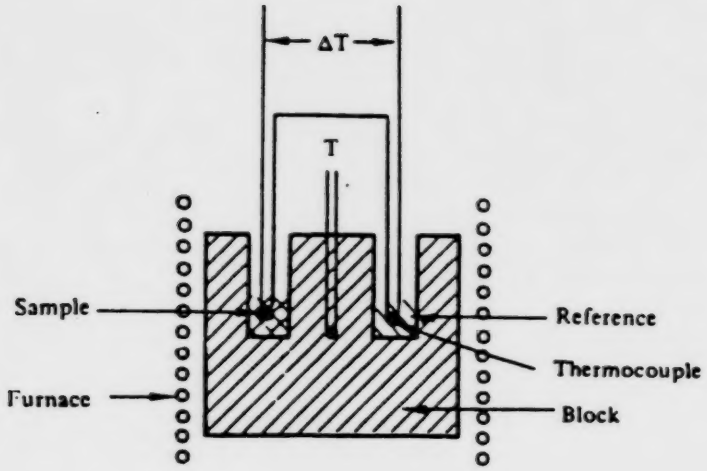
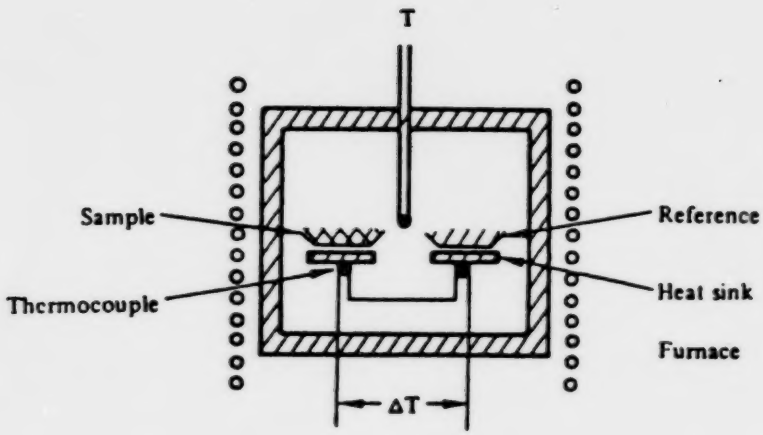


Figure A2 Adiabatic calorimetric curve for a 55 ppm H Zircaloy 2 sample. The solid line represents the heat capacity with hydrogen present and the points without hydrogen. The heat of dissolution for zirconium hydride was determined to be 38.6 kJ/mole H /3/.



(a) "CLASSICAL" DTA



(b) "CALORIMETRIC" DTA

Figure A3 Comparison of (a) classical DTA and (b) calorimetric DTA instruments [5]. Semi-quantitative results are only possible with classical DTA since the heat loss to the block is uncontrollable. Since thermocouples are present in the main heat loss path in calorimetric DTA, calorimetric quantitation is possible.

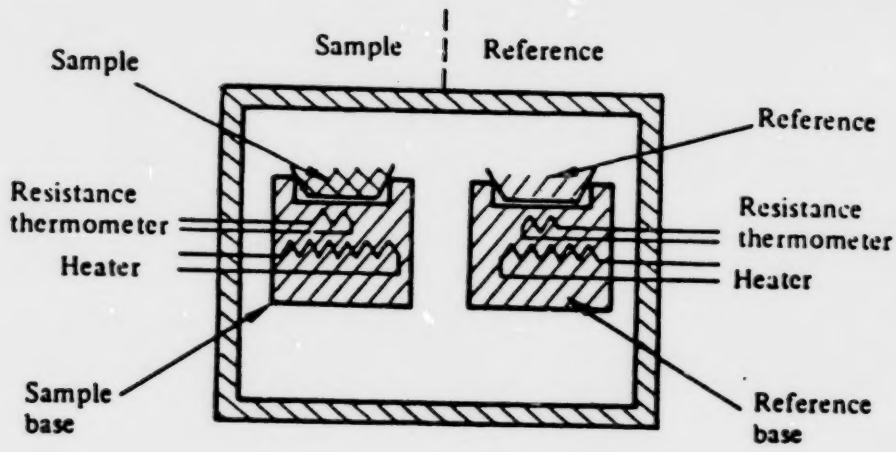


Figure A4 Schematic diagram of a DSC cell/5/ (Perkin Elmer). Auxiliary heaters maintain the temperature differential to zero while the difference in heat flow to each is monitored.

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